

Sequential Oxidative/Reductive Bleaching and Dyeing of Wool in a Single Bath at Low Temperatures

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ABSTRACT

A new bleaching and dyeing process applicable to wool involves a sequential oxidative/reductive bleaching combined with a subsequent dyeing in a single bath. Apart from dyebath bleaching processes in which the bleaching agent is added towards the end of the dyeing process when almost all the dye is exhausted, bleaching and subsequent dyeing are normally done in separate baths due to the sensitivity of the dyes to bleaching agents. In the latter process, it is important that all bleaching agents be thoroughly washed off before dyeing, because any residual bleaching agent (hydrogen peroxide, reductive bleach) may adversely affect the results. The newly developed single-bath process begins with an oxidative hydrogen peroxide bleaching followed by addition of thiourea to the residual hydrogen peroxide in the same bath. Thiourea dioxide formed by the resulting chemical reaction hydrolyzes in solution to sulfinate anion and urea. Sulfinate anion is a strong reducing agent and effects reductive bleaching. At the end of the reductive bleaching stage, a small amount of hydrogen peroxide is added to oxidize all the reductive sulfur species in solution to the sulfate anion, which together with the urea serves subsequently as a dye assist. Once the temperature of the bath is lowered, dyes may be added to the same bath. The new sequential single-bath bleaching/dyeing process results in much brighter pastel shades upon dyeing, due to better whiteness obtained initially with sequential oxidative/reductive bleaching. Furthermore, there is a reduction in processing time, temperature, and effluent compared with conventional procedures and the utilization of byproducts from the initial bleaching assists during the subsequent dyeing step.

Wool dyeing is a centuries-old art. An increasing understanding of the complex structure of the wool fiber has enabled us to pinpoint specific structural features through which dye diffusion takes place. This knowledge may in turn facilitate improvements in dyeing processes, leading to a product of very high quality.

Scoured wool varies in shade from the light cream of wools considered to have good color to discolored urine-stained wools and the near blacks of heavily pigmented wools. Since even the background natural color of wool interferes with dyeing to specific pastel or bright colors, all of these wools are bleached. Therefore, in order to achieve bright shades, one has to either bleach wool before dyeing or incorporate a bleaching agent

somewhere during the dyeing cycle. The former process calls for a lengthy treatment, since wool has to be bleached and free of any residual bleaching agent before it may be dyed successfully. The latter process, though promising, must take into account the sensitivity of some dyes to bleaching agents, hence limiting the number of dyes that may be used. Two main factors operating in the dyeing of bleached wool are the swelling of fibers, which results from disulfide scission caused by bleaching treatments, and the creation of negative charges on the surface, which may hinder dye adsorption and diffusion. Because these factors work against each other, a compromise has to be found where there is sufficient swelling caused by bleaching but at the same time considerably less negative charge created at the surface. This should be achievable by reducing the concentration of bleaching reagents and limiting the severity of the bleaching conditions, so that the factors above are maintained within limits to allow an acceptable dyed product. Also, the higher the concentra-

tion of bleaching agents and the more severe the bleaching conditions, the greater the whiteness. Therefore a balance must be achieved between optimum whiteness and good quality dyeing.

Lemin and Vickerstaff [11] have reported that hydrogen peroxide-bleached wool dyes to a weaker shade than unbleached wool, because both dye affinity and the number of dye sites available are reduced. Duffield [8] has described the Tubotex PC³ (mixture of sodium silicate and caustic soda with pH 9.0–10.0) prebleaching process; bright pastel shades from subsequent dyeing are fostered by this rapid, low temperature alkaline hydrogen peroxide bleaching (1 hour, 40°C, pH 9.0–10.0 using sodium silicate and caustic soda). This process has been used in several bleaching houses with improved results in terms of whiteness and residual fiber damage, owing to the low temperature of the process.

There are numerous scientific papers and patents on the simultaneous dyeing and bleaching of fibers [2, 4, 7, 9, 15, 17–19, 21–23]. Schmidt [17–19] has described simultaneous dyeing and bleaching of proteinaceous and other fibers, where the fibers are treated at elevated temperatures in a nonalkaline aqueous liquor that contains (a) an acid dye capable of dyeing wool but resistant to peroxides and (b) performic acid in the form of the reaction product of hydrogen peroxide and a performic acid precursor. Senner *et al.* [21] have reported that performic acid with a special stabilizer and hydrogen peroxide with the stabilizer Lufibrol W are very efficient bleaching agents in the single bath dyeing and bleaching of wool. Arsov *et al.* [2] have reported a satisfactory dyeing and bleaching process of wool yarn where the yarn is first dyed and then a solution containing hydrogen peroxide is added near the end of the dyeing to give bright shades. Nikolova *et al.* [15] have described a single bath dyeing and bleaching process of a 50:50 rayon-wool yarn in which the hydrogen peroxide is added to the dyebath after 20 minutes at the boil to obtain greater color purity and brilliance than yarn processed in the conventional two-bath method. Even though these single bath processes are reputed to give bright shades, they are rather limited because some of the dyes are sensitive to bleaching agents and so cannot be used. Uehara [22] discusses a single bath bleaching and dyeing process that calls for bleaching fibers in a bath containing urea peroxide as the major component, neutralizing the bath with NaHSO₃ after bleaching, and dyeing the fibers by adding the dye to

the same bath. In another patent, Uehara [23] reports a single bath bleaching and dyeing process for textiles in which the textile is bleached in a bath containing bleaching agent(s), chiefly peroxide(s), and the agents are decomposed by adding reducing agent, chiefly thio compounds, to the bath, followed by dye(s) added to the bath. In the example given in the patent, Uehara explains that the bath is drained and replaced by a fresh bath after neutralization of peroxide(s) with a reducing agent, followed by dyeing according to conventional methods. Other dyebath bleaching processes that employ products available commercially are summarized in a recent review by Duffield [9].

As far as the dyeing of wool alone is concerned, research has been aimed at producing level dyeings with minimum fiber damage. We strongly recommend to the reader a recent review by Lewis [12] on dyeing and wet processing of wool. The emphasis on dyeing of wool at the iso-ionic region (pH 3.5–4.5) for minimal fiber damage is particularly noteworthy, as it was once thought that dyeing at “neutral pH” was safe. Many dyes and dyeing auxiliaries have been offered commercially for good level color with minimal fiber damage [10, 14]. There has also been considerable effort to produce good exhaustion and level dyeings with minimal fiber damage at low temperatures (40–90°C), since dyeing at the boil not only causes excessive fiber damage but also yellowing, which hinders the brightness of dyed product [12]. Most of these low temperature dyeing processes are claimed to give adequate exhaustion with level dyeing and reduced fiber damage at 80–90°C, but it is not clear if any of them have ever been accepted commercially. A very recent article by Rippon and Harrigan [16] describes a promising new method for dyeing wool at 80–90°C. The method uses a simple pretreatment consisting of a scour under mildly alkaline conditions with a special surfactant (Sirolan LTA). The wool is then dyed from a fresh bath. The authors claim improved uniformity of dye uptake, dyeing rate, and degree of fiber penetration at temperatures below the boil, compared with untreated wool. Another low temperature (80–90°C) dyeing of protein and polyamide fibers, described by Bendak [5], uses a redox system. Bendak investigated dyeing on fibers with acid dyes having various *A*-values (ratio of organic to inorganic character) in the presence of a thiourea/hydrogen peroxide system in water or water/*n*-propanol (9:1). He claimed an increase in color intensity of the substrates dyed in the presence of the redox system, as well as rapid exhaustion of the dyebath. It is not clear, however, whether the association of the dye with the substrate involves covalent bonding

besides the usual salt linkages, and also whether there are any free radicals formed on both the substrate and the dye. There is also no mention of the redox potential of the dyebath. From the concentration of thiourea and hydrogen peroxide mentioned in the article, it seems that the dyebath would be reductive, which in turn would interfere with shades and colors of some dyes.

In this paper, we present a new approach for bleaching followed by dyeing of wool in a single bath. The bleaching part of the process is itself a sequential oxidative and reductive bleaching in a single bath, and we have reported the details of this now-patented process in an earlier paper (Arifoglu *et al.* [2]).

Experimental

The wool we used for laboratory trials was a yellowed flannel fabric (20.60–26.39 microns, 233 g/m²), kindly supplied by Forstmann and Co., Inc., Dublin, GA. The hydrogen peroxide was a 30% (w/w) aqueous solution. Thiourea⁴ and tetrasodium pyrophosphate decahydrate were obtained from Aldrich Chemical Co., Inc., Milwaukee, WI. Telon fast blue RLW (CI acid blue 204), Isolan red S-RL (CI acid red 414), and Avolan UL-75 (an amphoteric wetting and dye leveling agent) were kindly supplied by Mobay Corporation, Pittsburgh, PA. Avolan UL-75 has a dual role in the single bath bleaching and dyeing process: it acts as a wetting agent for the bleaching part of the process and is then carried over to the dyeing part of the process where it acts as a dye leveler. Lanaset violet B was kindly supplied by Ciba Geigy Corporation, Greensboro, NC. All other chemicals were of ACS grade.

BLEACHING TREATMENTS

The wool fabric was bleached in an Ahiba Texomat (Ahiba Inc., Charlotte, NC) laboratory dyeing apparatus. Redox potential was monitored on a voltmeter using a Corning platinum redox combination electrode (a high quality platinum sensing element and a sealed Ag/AgCl reference element; Fisher Scientific Co., Springfield, NJ); pH was monitored on an E & K pH meter (E & K Scientific Products, Saratoga, CA) using a Corning combination glass electrode (Fisher Scientific Co., Springfield, NJ). All laboratory bleaching trials were done at a liquor to wool ratio of 30:1. Wool samples (10 g) were bleached according to the sequence of stages outlined in Figure 1 for sequential bleaching and dyeing in a single bath. The alkaline H₂O₂ bleach-

ing of wool for subsequent dyeing in a separate bath was done as for A only, except that bleaching time was extended to 85 minutes and the wool was rinsed well, acid soured, and dried before dyeing. The sequential oxidative/reductive bleaching of wool for subsequent dyeing in a separate bath was done as outlined in Figure 1, except that at the end of the bleaching and neutralization cycle, the wool was taken out, rinsed, and dried before dyeing.

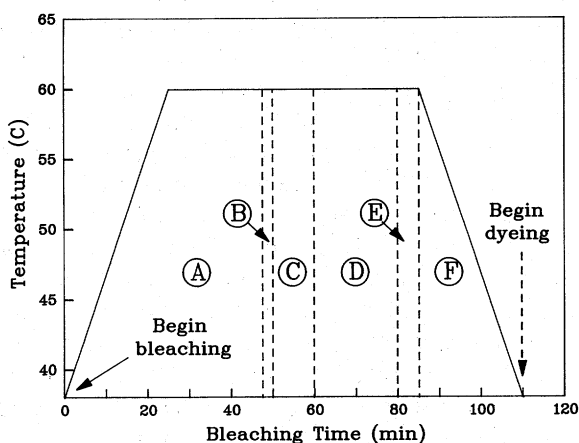


FIGURE 1. Temperature versus time chart for various phases of the sequential oxidative/reductive bleaching of wool up to dyeing in a single bath: (A) Alkaline bleach bath composition: 8.0 g/l H₂O₂ (30% w/w), 2.0 g/l tetrasodium pyrophosphate decahydrate, 0.167 g/l Avolan UL-75; pH of bleach bath initially = 9.4, pH of bleach bath at the end of stage A = 8.4. (B) 3 ml/l acetic acid (56%) is added to adjust pH to 5.0–5.5. (C) 1.67 g/l thiourea is added to react with residual hydrogen peroxide in the bath. (D) Sufficient aqueous ammonia is added to adjust pH to 6.8–7.2 to obtain the surge in potential to –640 mV for reductive bleaching. (E) 2.0 g/l acetic acid (56%) is added to adjust pH to 4.5–5.0. (F) 2.0 g/l H₂O₂ (30% w/w) is added to neutralize the reductive bleach as well as to assist in the reformation of the disulfide bridges as the temperature of the bath is cooled back to 38°C for subsequent dyeing operations.

DYEING TREATMENTS

Dyeings (0.3–0.6% on the weight of fiber) were done according to procedures outlined by the dyestuff manufacturers at a liquor to wool ratio of 30:1 on both untreated and bleached wool samples for comparison of dye exhaustion and levelness. The dyebaths contained 0.5% Avolan UL-75 and 10% Glauber's salt on the weight of fiber, though no Glauber's salt was added to the bath for the single-bath bleached and dyed sample. Dye exhaustion profiles were produced by continuous absorbance measurements of the dyes at their wavelength of maximum absorption (Telon fast blue RLW, λ_{max} 628 nm; Isolan red S-RL, λ_{max} 502 nm;

and Lanaset violet B, λ_{\max} 598 nm) by circulating the dye solution through a 1-cm quartz cell during dyeing and recording the digital readout from a Perkin Elmer LC-95 UV/visible spectrophotometer (Perkin-Elmer Corp., Norwalk, CT).

MEASURING WOOL PROPERTIES

Whiteness (ASTM E-313) and yellowness (ASTM D-1925) indices of undyed samples were measured with a Colorgard System 1000 tristimulus colorimeter (Pacific Scientific Co., Gardner Neotec Division, Silver Spring, MD). Samples were illuminated with a quartz halogen lamp at a color temperature of 2854 K with 360° circumferential illumination (CIE Source C illuminant, CIE 1931 standard 2° observer) at a 45° angle from the sample's normal direction, with sample viewing at 0°. Color measurements on dyed samples were made on a Color Machine (also Pacific Scientific), which measures CIELAB CIE 1976 L^* a^* b^* color space and ΔE ; samples were illuminated with circumferential illumination (CIE Source C illuminant, CIE 1964 standard 10° observer) at a 45° angle from the sample's normal direction, with sample viewing at 0°.

Wet tensile strength of the wool flannel, bleached and dyed under various conditions, was measured according to the standard method [3]: the fabric was cut into five equal strips 140 mm long and 13 mm wide. These samples were then soaked for 24 hours in an aqueous solution containing Triton X-100 (0.5 g/l). An Instron tensile testing machine (Instron Corp., Canton, MA) with a 90 mm gauge length and a 23 kg ("50 lb") load cell was used to measure breaking load. The wetted out samples were secured between the clamps, and a constant load rate was applied along each strip until it broke.

Results and Discussion

The results of preliminary experiments have led to the following findings: Only an amphoteric wetting agent should be used in the process, as other wetting agents—nonionic, anionic, and cationic—may interfere with subsequent dyeing in the single bath bleaching and dyeing process. Although a nonionic wetting agent (Triton X-100) leads to complete exhaustion of dye at low temperatures (80–90°C), the dyeings suffer from the so called "drain effect," where the adsorbed dye desorbs when the dyed goods are rinsed in cold water. The mode of action of amphoteric wetting and leveling agents as dye levelers is best explained by their reversible complex formation with the dye. Hence only a fraction of the dye is made available to the fiber, de-

pending on the temperature of the dyebath. As the temperature is raised, more dye is released from the leveling agent/dye complex into the dyebath, where it is then free to interact with the fiber. The presence of high amounts of amphoteric dye leveling agent in the bath does not allow adequate exhaustion of the dye onto the fiber at low temperatures (80–90°C) because not all the dye is released at such temperatures. Therefore the amount of leveling agent must be carefully calculated so that adequate exhaustion of dye on the fiber is achieved at 80–90°C. Our preliminary experiments have shown that up to 0.5% Avolan UL-75 (on the weight of fiber) may be successfully used to yield good exhaustion at low temperatures.

Bleaching agent concentration is also critical if the dyeing process is to follow the bleaching process in the same bath. The reason for this is that the higher the amount of hydrogen peroxide used, the higher the amount of reductive bleach formed *in situ* and hence the higher the amount of sulfate anion formed as a result of neutralization of reductive bleach prior to dyeing. Sulfate anions have been used [6] as dye leveling and retarding agents in dyeing wool. They originate from Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), which is added to the dyebath to the extent of 0–20% on the weight of wool. Preliminary experiments show that 5–10 g/l H_2O_2 (30% w/w) is a good concentration range for adequate bleaching and dyeing processes. When the bleaching solution initially contains 8.0 g/l H_2O_2 (30% w/w), then the calculations (based on the amount of sulfate anion precipitated as barium sulfate by acidified barium chloride) show that there is 10–20% Glauber's salt present in the bath during dyeing. The amount of sulfate anion formed in the bath is directly related to the initial amount of thiourea added to the bath in the bleaching cycle. Efficient, effective bleaching may be obtained with thiourea levels less than the amounts mentioned in our earlier paper [1]. A molar ratio of 3:1 hydrogen peroxide to thiourea is appropriate and presents no danger of excess thiourea in the solution later to be discarded.

We incorporated the findings on amounts of leveling agent and thiourea into a protocol for combined oxidative/reductive bleaching (with or without subsequent dyeing) in the same bath. The effectiveness of the bleaching process (without dyeing) as measured by whiteness and yellowness indices and breaking loads is presented in Table I (sample S2), along with results from a parallel experiment without reductive bleaching (S1). Breaking loads are presented in Table I for samples bleached as per S1 or S2 and subsequently dyed; the full protocol of single-bath oxidative/reductive

bleaching with subsequent dyeing in the same bath is represented by protocol S5.

TABLE I. The effect of different bleaching and dyeing treatments on the breaking load and optical properties of wool flannel.

Sample ^a	Whiteness index ^b	Yellowness index ^c	Breaking load, N ^d
Untreated	-2.18 ± 0.31	31.60 ± 0.10	37.44 ± 2.32
S1	17.30 ± 0.30	23.14 ± 0.07	41.60 ± 2.10
S2	24.11 ± 0.23	20.11 ± 0.08	40.20 ± 1.78
S3	-	-	40.84 ± 1.87
S4	-	-	39.08 ± 1.54
S5	-	-	43.90 ± 2.37
S6	-	-	42.33 ± 0.47

^a S1: As per Figure 1, A only, experimental section, except that bleaching duration is for 85 minutes. S2: as per whole process (A-F) in Figure 1, experimental section (no dyeing). S3: as per S1, but dyed with Telon fast blue RLW at 80°C in a fresh bath. S4: as per S2, but dyed with Telon fast blue RLW at 80°C in a fresh bath. S5: as per S2, but dyed with Telon fast blue RLW at 80°C in the same bath. S6: untreated wool dyed with Telon fast blue RLW at 80°C. ^b As per ASTM E-313; mean value ± standard deviation of three samples, each having eight measurements. ^c As per ASTM D-1925; mean value ± standard deviation of three samples, each having eight measurements. ^d As per IWTO-4-60; mean value ± standard deviation of five samples.

Table I clearly shows that a whiter product is produced using the sequential oxidative/reductive bleaching (S2) rather than the alkaline H₂O₂ bleaching alone (S1), and that the tensile strengths of the wool flannel products are very comparable. Since we have a whiter product at the end of the bleaching cycle, the dyed product ought to look brighter. Note that the neutralization step, *i.e.*, the addition of a small amount of hydrogen peroxide following reductive bleaching (Figure 1, F), is very important for the reformation of disulfide linkages to preserve the strength of wool, as well as to get rid of any residual reductive bleach remaining in solution or on the wool.

Figure 2 presents a simplified drawing of the effect of bleaching agents on wool cystine residues (structure I). Under alkaline oxidative bleaching, wool fibers are attacked mainly at the disulfide bridges, resulting in irreversible formation of cysteic acid residues (II). The longer the wool is in contact with alkaline oxidative bleach, the greater the number of cysteic acid residues formed (III). Under the same conditions, some alkaline peptide bond hydrolysis also occurs (not shown in Figure 2). In the sequential oxidative/reductive bleaching process, oxidative bleaching (II) is prematurely curtailed when the bath is converted to a reductive medium. Here, more disulfide bridges are attacked by the

reductive bleach, but the scission mechanism of disulfide bonds is unsymmetrical and reversible, giving rise to cysteine and S-sulfocysteine (Bunte salt) residues (IV). The sulfitolysis reactions of wool with many reducing agents have been extensively studied and reviewed [13]. The presence of Bunte salt arising from reductive bleaching has been confirmed by FT-IR spectroscopy [20]. As for the reactions in solution, the decomposition of hydrogen peroxide in solution during alkaline oxidative bleaching is very small, owing to the presence of stabilizers such as pyrophosphate. Thiourea dioxide formed in solution by the reaction of hydrogen peroxide with thiourea is rather stable and only hydrolyzes under heat and neutral or alkaline conditions to yield sulfinate anion, which is the actual reductive bleaching agent. The other hydrolysis product is urea, which is carried over into the dyeing cycle. The neutralization step of the process (Figure 1, F) plays the most important part, as it is not only needed to fully oxidize the reductive bleach in solution but is also essential in the reformation of the disulfide residues (Figure 2, V) to preserve the strength of fibers as well as to lower the electrostatic repulsion between the negative charges on the fiber and the dye anions in a subsequent dyeing process. Figure 2 shows that under carefully controlled conditions, disulfide bonds are reformed (V) from cysteine and S-sulfocysteine residues under mild oxidation conditions. The reductive bleach in solution is also fully oxidized with dilute hydrogen peroxide to yield sulfate anions, which in turn serve as a dye assist.

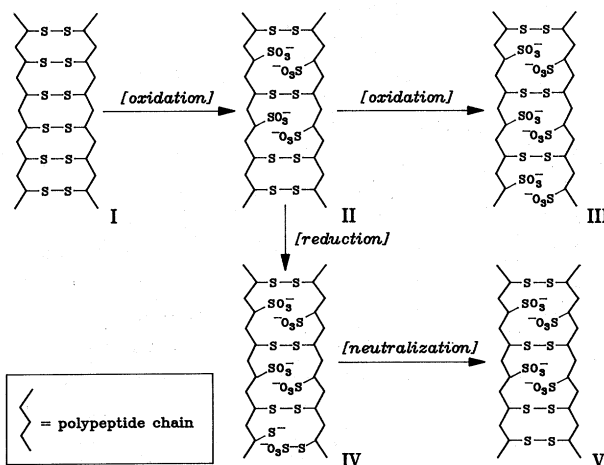


FIGURE 2. Schematic presentation of possible reactions of disulfide residues in wool with oxidizing and reducing agents.

We have used three different kinds of acid dyes to demonstrate the effectiveness of single bath bleaching and dyeing over other treatments. In these investigations, we have studied only pastel dyeings (0.3–0.6% on the weight of fiber), because the effect of bleaching on the overall brightness of color plays the most important role there. The results of these investigations are depicted graphically in Figures 3–5. Generally we see that the exhaustion of the dyes on wool is higher for the single bath bleaching and dyeing process than the other processes. There are a few possible explanations of this: First, as previously mentioned, one of the end products of the sequential oxidative/reductive process is urea, which may somewhat disaggregate the dyestuff in solution as well as assist in further swelling of wool, hence allowing easier diffusion of dye into the wool fiber. Second, wool that has undergone a sequential oxidative/reductive bleaching has been well wetted out throughout the bleaching treatment, and this carries over to the dyeing stage when wool is not taken out of the bleach bath. Third, we believe that since the alkaline oxidative bleaching with H_2O_2 has been interrupted at an earlier stage to accommodate the reductive bleaching stage in the given time frame, there is less formation of cysteic acid. Cystine that has undergone reductive cleavage by sulfinate anion during the reductive

bleaching stage may be restored efficiently by dilute hydrogen peroxide. The dual bleaching process, then,

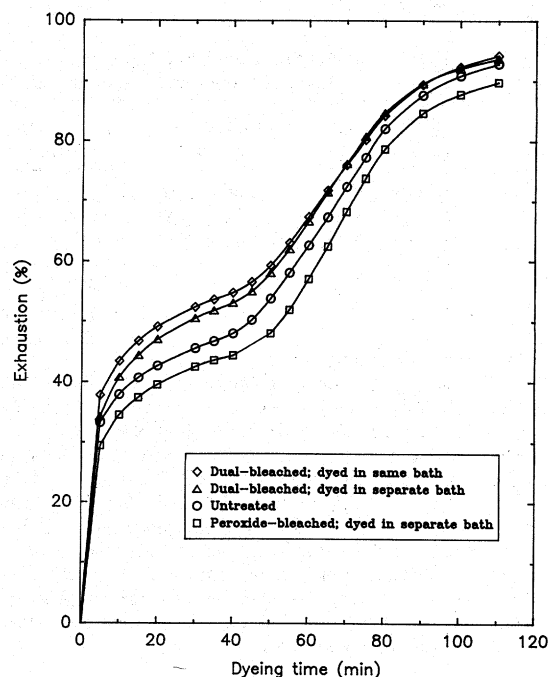


FIGURE 4. Exhaustion profiles of Isolan red S-RL (0.3% owf) dyestuff with time on untreated and various bleached wools.

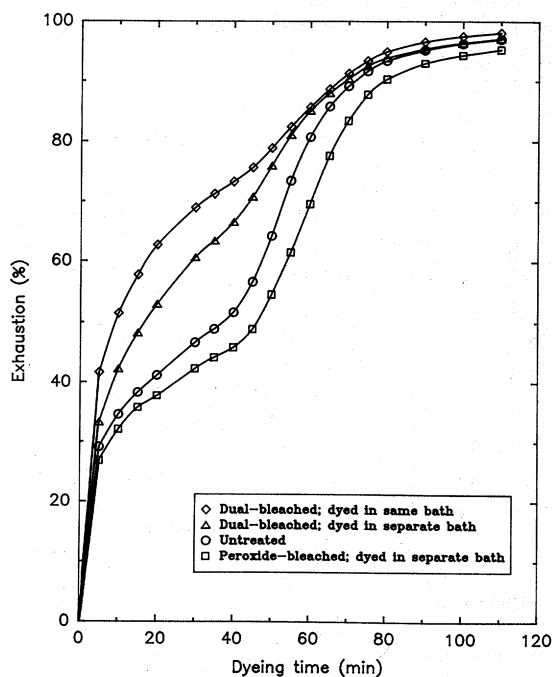


FIGURE 3. Exhaustion profiles of Telon fast blue RLW (0.6% owf) dyestuff with time on untreated and various bleached wools.

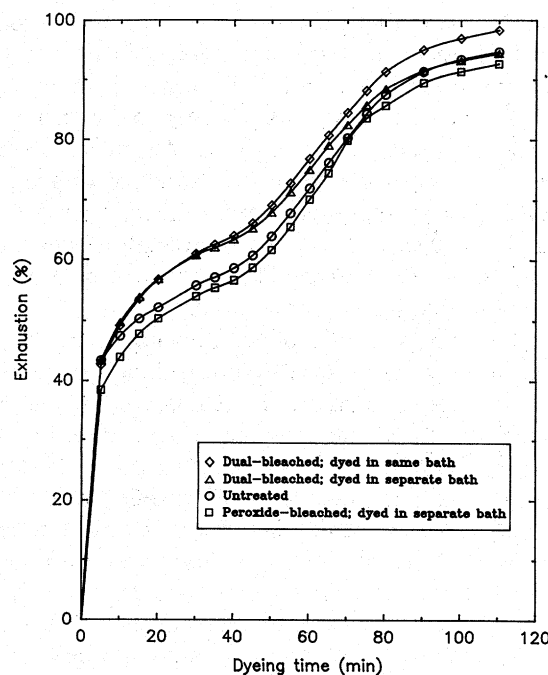


FIGURE 5. Exhaustion profiles of Lanaset violet B (0.3% owf) dyestuff with time on untreated and various bleached wools.

gives rise to good exhaustion owing to sufficient swelling and considerably reduced repulsion of dye anions by the presence of cysteic acid groups on the surface and in the interior of wool fiber.

CIELAB and ΔE color measurements are presented in Table II for samples bleached by different regimens and then dyed with Telon fast blue RLW. The blue color of the dye, which is somewhat blue-violet instead of blue-green, is most noticeably affected by the yellowness of the underlying fabric. When we compare b^* values (yellowness/blueness; the more positive, the yellower), the yellowness of the dyed samples diminishes, progressing from use of unbleached fabric (S6) through peroxide-bleached (S3) through dual-bleached (S5/single-bath; S4/separate dye bath). L^* values (lightness/darkness) are similar but for the peroxide-bleached sample (S3); its higher value we believe is due to less dye uptake than the other samples. Differences in yellowness and dye uptake are plainly visible to the eye for all sets of dyed samples and support the use of the dual-bleaching processes prior to dyeing.

TABLE II. CIELAB and ΔE measurements of wool samples dyed with Telon fast blue RLW.

Sample code ^a	L^*	a^*	b^*	ΔE
S6	50.12	-0.50	-35.81	-
S5	50.54	1.40	-38.87	3.64
S4	50.70	1.63	-39.17	4.03
S3	51.28	0.71	-37.47	2.37

^a As per Table I.

Conclusions

We have developed a combined oxidative/reductive bleaching and dyeing process for wool in a single bath as an improved alternative to conventional bleaching and dyeing processes. Brighter and deeper pastel shades may be obtained with this new process, since less chemical damage to the wool fibers allows higher dye exhaustion and affinity than is achievable on conventional hydrogen peroxide bleached samples of similar whiteness. This process not only reduces the total treatment and machinery use time, but also greatly reduces the effluent since it is done in a single bath. The new process in all its variations is the subject of a patent application [1].

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an assembly for measuring continuous dye absorption, and Mr. Stephen L. Wildman for the tensile strength tests.

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